OR-7

DIPYRAZOLODIOXADIAZOCINES AS EASILY STORABLE AND "READY TO USE" PRECURSORS FOR IN SITU GENERATION OF ENOLATE-IMINIUM 1,4-DIPOLES: AN ATOM-ECONOMICAL APPROACH TOPYRAZOLO[5,1-d][1,3,5]DIOXAZINES

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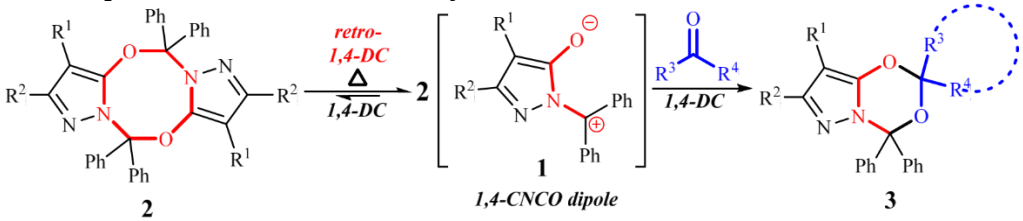
Abstract. During the past few decades dipolar cycloaddition reactions have become a powerful and effective tool for the synthesis of a wide range of heterocyclic compounds. In particular, the 1,3-dipolar cycloaddition reactions are successfully used in organic and medical chemistry to obtain a variety of five-membered heterocycles and the total synthesis of natural and biologically active products.[1,2]. However, in sharp contrast, there is relatively little reported information on 1,4-dipolar cycloaddition reactions, despite the fact that the basic principles of such processes were proposed by R. Husgen almost half a century ago. In this regard, over the past two decades, 1,4-dipolar cycloaddition reactions are the subject of considerable research attention and, along with the Diels – Alder 4+2-cycloaddition, offer unique and alternative methods for producing six-membered heterocycles.[3].

For the first time we have discovered a simple and highly efficient method for the generation of cyclic enolate-iminium 1,4-dipoles.[4] **1***via* unique thermal decomposition of easily available dipyrazolodioxadiazocines **2**. By this approach various substituted spiro pyrazolo[5,1-*d*][1,3,5]dioxazines **3** have been synthesized by unusual cycloconversion of dipyrazolodioxadiazocines in the presence of ketones with overall high yields (up to 85% yield). Moreover, the developed method is 100% atom economical and proceeds under metal-catalyst- and solvent-free conditions.



Scheme 1. Cycloconversion of dipyrazolodioxadiazocines in the presence of ketones

References

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